

# Unusual magnetic relaxation behavior in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

J. López\*, P. N. Lisboa-Filho, W. A. C. Passos, W. A. Ortiz and F. M. Araujo-Moreira

*Grupo de Supercondutividade e Magnetismo,*

*Departamento de Física, Universidade Federal de São Carlos, Caixa*

*Postal - 676, São Carlos, SP, 13565-905, BRAZIL,*

*pjlopez@iris.ufscar.br*

## Abstract

We present an extensive study of the time dependence of the magnetization in a polycrystalline and low temperature charge ordered  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample. After application and removal of a 5 T magnetic field, a systematic variation of the magnetic relaxation rate from 10 K to 245 K was found. At 195 K, the magnetization decreases in a very short time and after that it increases slowly as a function of time. Moreover, between 200 and 245 K, an increase in magnetization, above the corresponding value just after removing the 5 T magnetic field, was measured. This unusual behavior was tested in several other relaxation procedures.

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The low temperature charge ordered compound  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  has been intensively studied in the last years due to its very large variations in resistivity, magnetization, and lattice parameters as a function of temperature, magnetic field and isotope mass<sup>1,2,3</sup>. Besides, this compound is particularly interesting due to the coexistence and microscopic separation of two phases at low temperatures: one ferromagnetic and one antiferromagnetic<sup>4</sup>. Recently, Huang et. al.<sup>5</sup>, measured neutron powder diffraction and magnetization in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  samples, with  $x=0.47$ ,  $0.50$  and  $0.53$ . They argued the existence in all samples of a paramagnetic-ferromagnetic transition, for a phase called F-I, at 265 K and the formation

of a second crystallographic phase, named A-II, below 230 K. They also pointed out that phase A-II ordered antiferromagnetically with a CE-type magnetic structure below 160 K<sup>5</sup>. Moreover, Radaelli et. al.<sup>1</sup> measured a rapid change of the lattice parameters between 130 K and 225 K in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ . This was associated with the development of a Jahn-Teller distortion of the Mn-O octahedra, as well as partial orbital ordering.

Relaxation experiments are a useful tool to study the dynamics of the charge ordering phase due to the frustration in the spin equilibrium configuration. Until now, attention has been focused in the relaxation of electrical resistivity after a large change of an applied magnetic field, which induces a transition from a ferromagnetic metallic state to a charge ordered insulator phase or conversely<sup>6,7</sup>. However, systematic reports of magnetic relaxation curves ( $M(t)$ ) in charge ordered compounds are rare, possible because the abrupt jump seen in resistivity is absent in magnetic measurements. Here, we present an extensive study  $M(t)$  curves measured in a polycrystalline sample of  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ . We also performed similar measurements in a polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  sample for comparison.

Polycrystalline samples of  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  and  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  were prepared by the standard procedures described elsewhere<sup>8,9</sup>. X-ray diffraction measurements pointed out high quality samples. Magnetization measurements were done with a standard MPMS-5S SQUID magnetometer. The relaxation measuring procedure was the following: first, the sample was heated to 400 K in zero magnetic field; second, the remanent magnetic field in the solenoid of the SQUID magnetometer was seted to zero; third, the sample was cooled down to the working temperature in zero magnetic field; fourth, an applied magnetic field ( $H$ ) was increased from 0 to 5 T at a rate of 0.83 T/minute and remained applied for a waiting time  $t_w=50$  s; fifth,  $H$  was decreased to zero at the same rate; finally, when  $H$  was zero (we defined this moment as  $t=0$ ) the  $M(t)$  curve was recorded for more than 210 minutes. We have measured the profile of the remanent magnetic field trapped in the superconducting solenoid after increasing  $H$  to 5 T and the subsequent removal. Within the experimental region the trapped magnetic field was lower than 1.1 mT.

Figure 1 shows the temperature dependence of the magnetization measured with  $H=5$

T for one of the  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples studied. The inset shows the same type of measurement with  $H=1.2$  mT. In the first case the measurement started at 2 K after a zero field cooling procedure, while in the second (inset) started at 400 K. The large hysteresis, at magnetic field as high as 5 T, is a clear evidence of the intrinsic frustration in the equilibrium configuration of the spin system. The paramagnetic-ferromagnetic transition around 225 K (minimum slope) is independent of the applied field and the followed path. However, the transition to the antiferromagnetic phase is path dependent and the Neel temperature ( $T_N$ ) decreases with the increase of  $H$ . Values of  $T_N$ , calculated from the maximum slope in the curves, changed between 100 and 195 K. The shape of these curves is in agreement with previous reports in the literature<sup>3,10</sup>.

Figure 2 shows magnetic relaxation measurements from 145 K to 195 K. To facilitate the comparison between curves at different temperatures, the magnetization in each case has been normalized to the corresponding value just after removing the  $H=5$  T. We will denote these curves as  $m(t)=M(t)/M(0)$ . As could be seen, the relaxation rate (mean slope of the curves or  $\Delta m/\Delta t$ ) increases systematically with increasing temperatures from 150 K to 195 K. It is important to note that slopes here are negatives. The ratio of magnetization change between  $t=\infty$  (the last measurement made) and  $t=0$ ,  $m(\infty)$ , at 150 K is about 20 %, while at 195 K is only 0.9 %. The increase in the relaxation rate between 150 and 195 K is in clear contrast with the behavior between 10 K and 150 K, where the relaxation rate decreases<sup>11</sup>. Included in figure 2 is the curve corresponding to 145 K which illustrates this behavior. Measurements of  $M$  versus  $H$  for this system<sup>3,11</sup> revealed the complete destruction of the antiferromagnetic phase above 150 K with  $H=5$  T. This fact could be influencing the change of behavior of the relaxation rate around 150 K.

The inset in figure 2 reproduces the relaxation curve before normalization for 195 K. This curve is noticeable different from those at lower temperatures. Here, the magnetization first decreases and, after approximately 4 minutes, starts increasing with time. The inset in figure 3 also shows the  $M(t)$  curves at 200 K. In this case, no decrease in magnetization was measured, but a monotonous increase with time (approximately  $62 \cdot 10^{-5} \mu_B$  in 218

minutes) is observed. The experiment at 200 K was repeated with a sample of the same compound having only 9 % of the original mass. A similar increase of magnetization with time ( $88 \cdot 10^{-5} \mu_B$  in 218 minutes) was found. These values are about 10 times smaller than the magnetization measured with  $H=1.2$  mT at the same temperature (see inset in figure 1).

The main frame of figure 3 shows  $m(t)$  curves from 195 K to 245 K. Notice that, differently from the previous figure, all curves, except the one at 195 K, show values above one. In other words, the magnetization increases with time (curves have positive slopes) above the  $M(0)$  value in each case. Furthermore,  $m(\infty)$  values are systematically higher with higher temperatures: from 0.9 % at 195 K to 75 % at 240 K. However,  $M(0)$  decreases with higher temperatures, as shown in figure 1. The curve at 245 K is also shown and presents a smaller  $m(\infty)$  value with respect to the one at 240 K, probably associated with the transition of the system to the paramagnetic phase. Magnetic relaxation measurements were also done between 245 K and 350 K. In this temperature interval we did not find a systematic variation of the relaxation rate. Nonetheless, above 260 K, the  $M(t)$  curves always show the usual decreasing behavior with time.

As a small magnetic field is trapped (typically about 1 mT) in the superconducting solenoid of the SQUID magnetometer, resulting after successive applications and removals of  $H=5$  T, we decided to check its role in the unusual increase in magnetization. The temperature of 210 K was chosen since the absolute value of magnetization is not too small and the increase in normalized magnetization is higher than at 200 K. We repeated the standard relaxation procedure, but instead of changing the applied magnetic field from 5 T to  $H=0$  mT (squares), we reduced it from 5 T to  $H=-1.2$  mT (circles) and  $H=-10$  mT (triangles in the inset). In each case, this last field remained applied during the whole relaxation measurement. For  $H=-1.2$  mT the actual field applied to the sample is almost zero. The initial magnetization of the sample here is lower than in the  $H=0$  mT case, but it is still positive. However, the  $H=-10$  mT is about 10 times higher than the trapped flux in the SQUID solenoid and the actual applied field to the sample is negative. The

initial magnetization of the sample is lower with  $H=-10$  mT than in the previous cases and has a negative value (see inset). Note that, contrary to what it is usually expected, the magnetization increases with time even with applied negative magnetic fields. The last measurements strongly support the point that is not the small trapped magnetic field in the solenoid of the magnetometer which is causing the unusual relaxation in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ .

Next, we repeated the standard relaxation procedure changing  $t_w$ . Figure 5 shows three  $m(t)$  curves with  $t_w$  equal to 50 s (squares), 500 s (circles) and 5000 s (up triangles). Clearly, the normalized increase in magnetization is higher the longer the 5 T magnetic field remains applied. Values of  $M(0)$  also increase for longer  $t_w$ . A plausible explanation could be that the remanent trapped field in the sample after removing the  $H=5$  T, which is higher for longer  $t_w$ , is causing the self-alignment of the spins and the increase in magnetization. Therefore, these curves would be reflecting information about the interactions in the  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample.

Finally, we repeated the standard relaxation procedure for a  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  polycrystalline sample. The ground state of this composition is a single ferromagnetic phase with the paramagnetic-ferromagnetic transition around 250 K. The magnetization, in relaxation measurements both above and below the Curie temperature, always decreased with time. These results for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  are in agreement with a similar study reported for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ <sup>12</sup>.

We conclude that is not only the ferromagnetic interaction that is causing the increase in magnetization in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ . In order to understand this behavior we have to include other specific details of the crystalline and magnetic structure of the charge ordered material. These intriguing results could be a consequence of the competition between ferromagnetic double exchange and antiferromagnetic superexchange coupling. However, further studies in other charge ordering compounds, as well as simultaneous measurements of magnetization, resistivity, etc. are desirable to elucidate this unusual behavior.

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Figure 1. Magnetization per Mn ion versus temperature measured with an applied

magnetic field of 5 T (1.2 mT in the inset) for a  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample. Magnetization is given in Bohr magnetons per manganese ion. Arrows and numbers show the direction of temperature sweep.

Figure 2. Normalized magnetic relaxation measurements after applying and removing an applied magnetic field of 5 T. Time is shown in logarithmic scale. The large arrow indicates the direction of increasing temperatures and relaxation rates (slope less negative) between 150 K and 195 K. Also shown is the curve for 145 K that presents a higher relaxation rate in comparison with 150 K. The inset reproduces details of the curve at 195 K with the corresponding error bars.

Figure 3. Normalized magnetic relaxation measurements after applying and removing a magnetic field of 5 T. Time is shown in logarithmic scale. The large arrow indicates the direction of increasing temperatures between 195 K and 240 K. Also shown is the curve for 245 K that presents a smaller increase of the normalized magnetization. The inset reproduces details of the curve at 200 K with the corresponding error bars (same dimension of circles), showing an unusual increase in the magnetization.

Figure 4. Magnetic relaxation curves at 210 K after repeating the standard procedure but reducing the field from 5 T to  $H=0$  mT (squares),  $H=-1.2$  mT (circles) and  $H=-10$  mT (triangles in the inset). The initial magnetization of the sample decreases with increasing negative magnetic field and all curves show an increase in magnetization with time. Error bars are of the same dimension of symbols for all curves.

Figure 5. Normalized magnetic relaxation measurements at 210 K after applying a 5 T magnetic field, keeping it for a waiting time  $t_w = 50, 500$  and  $5000$  s, and removing it. The increase in normalized magnetization is higher the longer the magnetic field remains applied.

Figure 1, J. Lopez et. al.

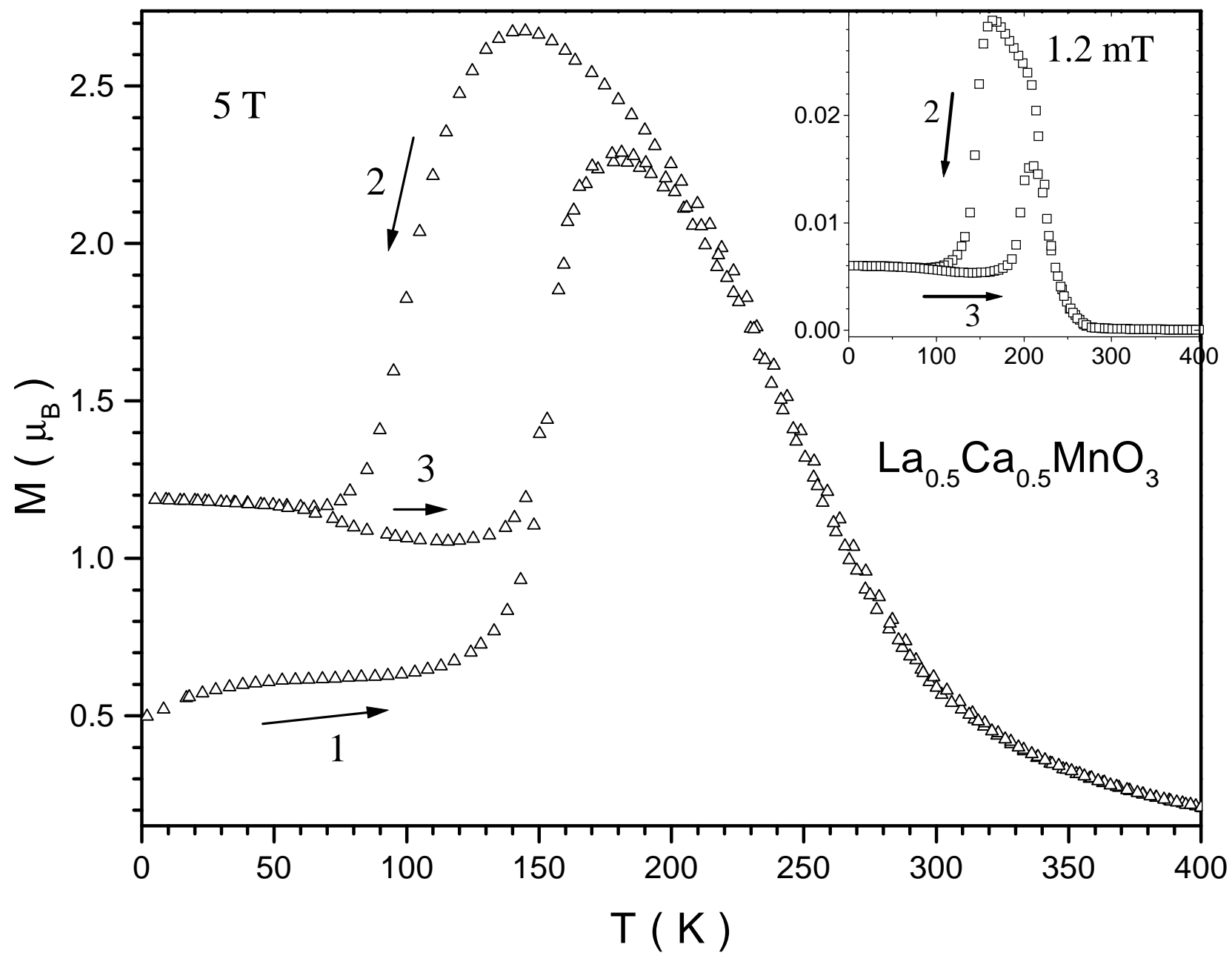




Figure 2, J. Lopez et. al.

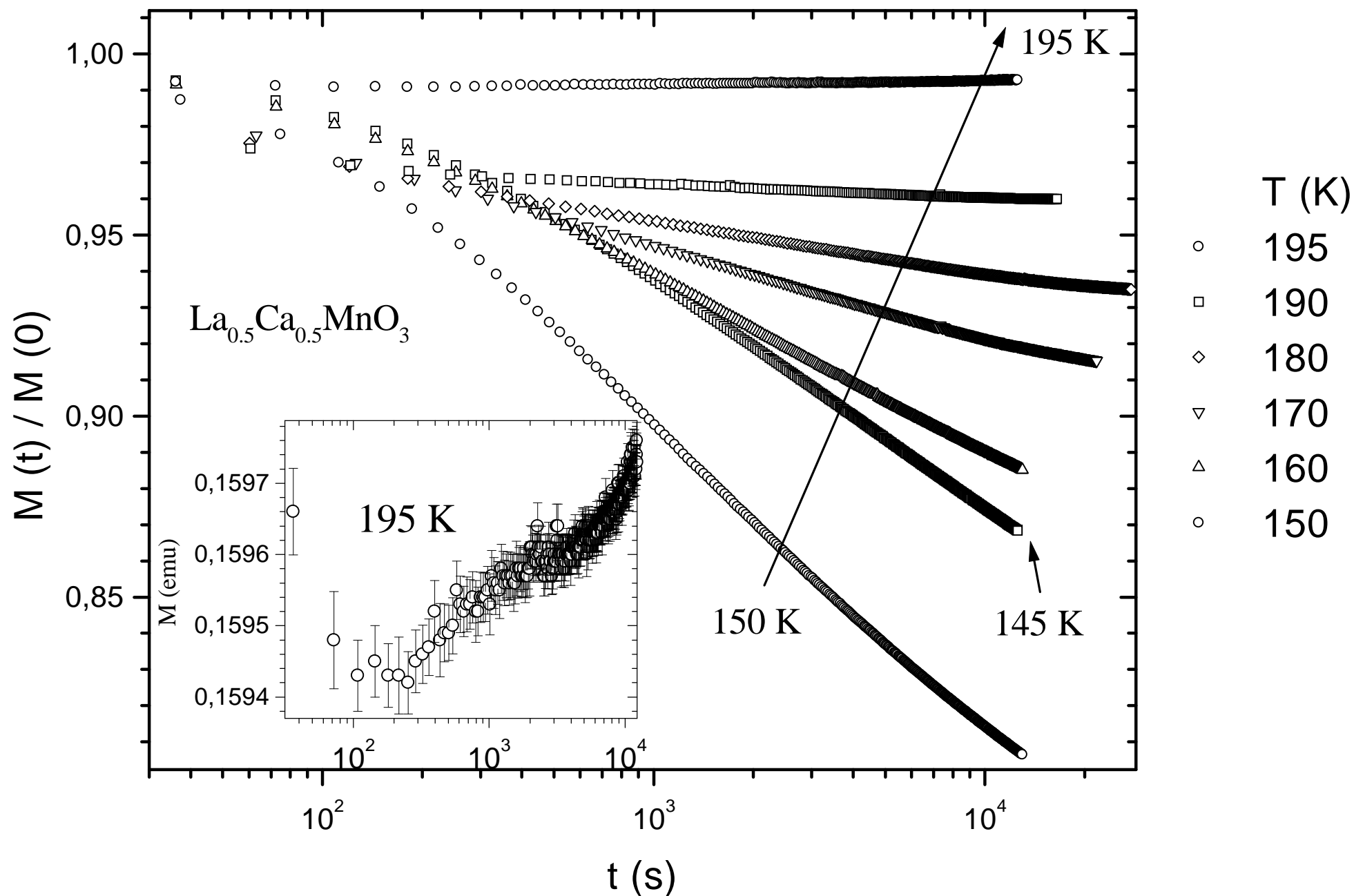


Figure 3, J. Lopez et. al.

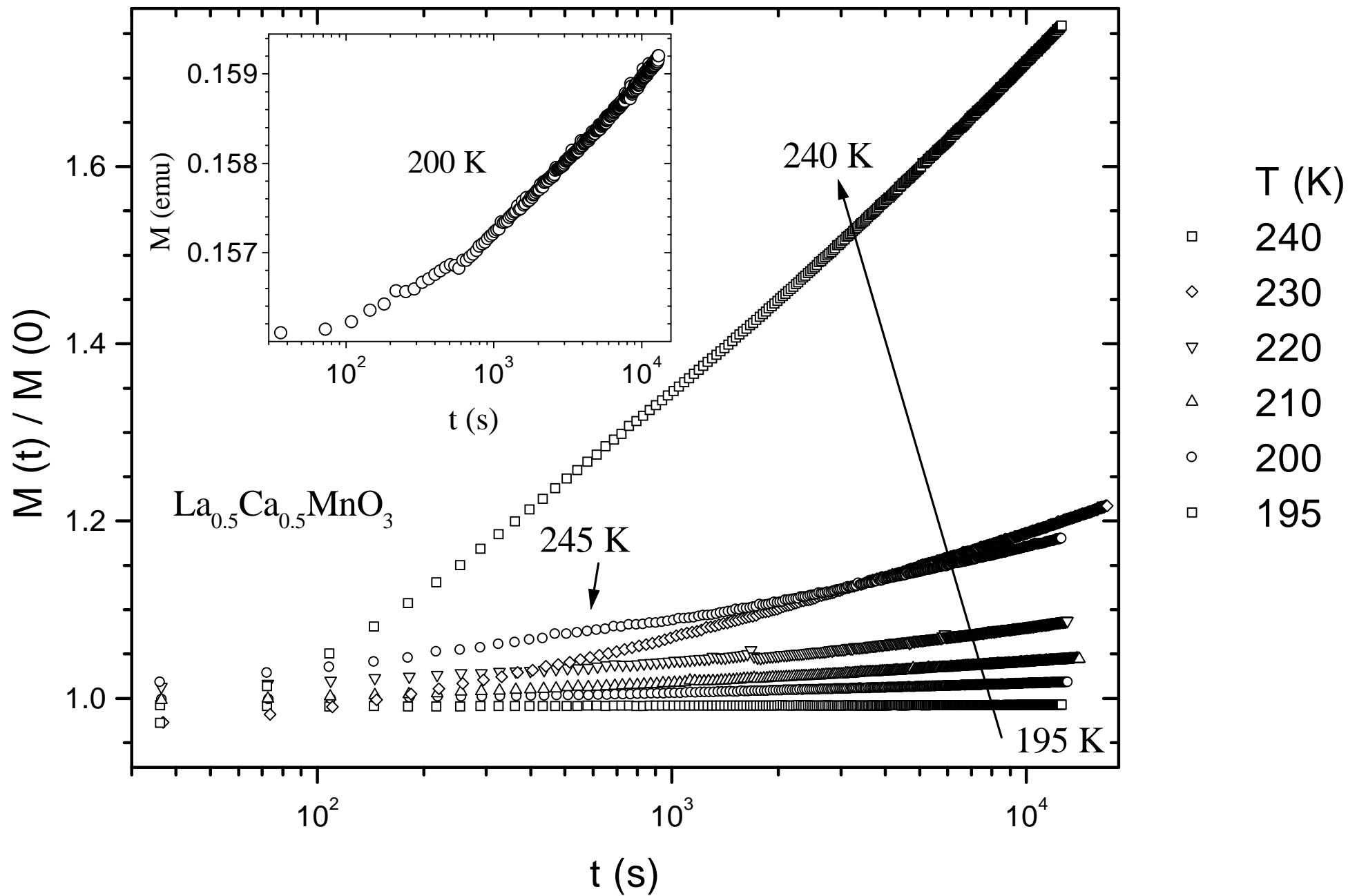


Figure 4, J. Lopez et. al.

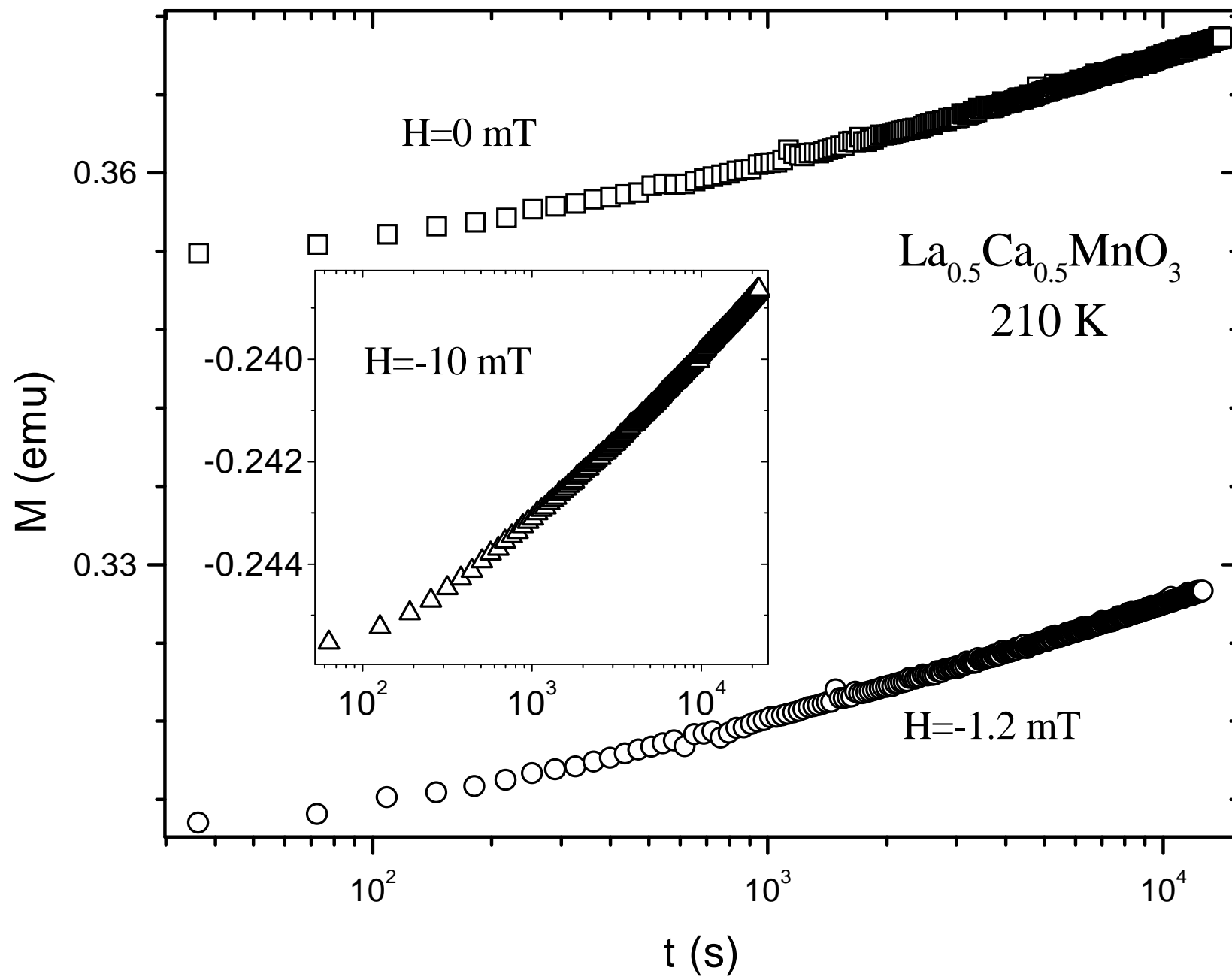


Figure 5, J. Lopez et. al.

